



Improved Mechanical Integrity of ALD-Coated Composite Electrodes for Li-Ion Batteries

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Mechanical properties of MoO₃ composite anodes coated with Al₂O₃ by atomic layer deposition (ALD) were examined using nanoindentation and nanoscratching. Significant improvement in adhesion to the current collector for the ALD-coated MoO₃ is observed. This improved adhesion enables enhanced electrical conductivity for these high capacity/high volume expansion materials, suggesting the potential of these coatings for high-energy density Li-ion batteries suitable for vehicular applications.

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High capacity anode materials for Li-ion batteries, such as silicon,¹ iron oxide,² and molybdenum oxide,^{3,4} suffer from rapid capacity fade due to detrimental changes in volume during lithium insertion and extraction. Material expansion/contraction can cause displacement of electrode materials, resulting in loss of electronic conductivity. Research efforts to circumvent fracturing due to volume expansion include employing nanostructured arrays,¹ carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) binders,⁵ and heat-treatment,⁶ as well as carbon-based matrices.⁷ However, many of these methods may be quite difficult to scale for Li-ion battery production for vehicular applications. In our previous work, we showed considerable improvement in the cycling stability, especially at a high rate, for high capacity nano-MoO₃ in an electrode fabricated with a conventional binder and conductive additive that are suitable for vehicular applications. This was achieved using a simple atomic layer deposition (ALD) process that is amenable to roll-to-roll manufacturing.⁸ Here, we conclusively demonstrate enhanced mechanical and physical properties of the ALD-coated electrodes with nanoindentation and nanoscratch techniques.

The composite electrodes (15 μm thick) were composed of nano-MoO₃, acetylene black, and poly(vinylidene fluoride) (PVDF) binder on 20 μm thick copper foil. The nano-MoO₃ hot-wire chemical vapor deposition synthesis and electrode fabrication⁴ have been described previously. In post-fabrication, the electrodes were coated with 4 monolayers of Al₂O₃ (~ 8 Å) with ALD.⁸ Both indentation and adhesion scratch tests were performed at room temperature on an MTS NanoIndenter XP with a standard triangular pyramidal Berkovich diamond indenter (maximum load = 500 mN, resolution = 50 nN). The electrodes were mounted on an aluminum holder with a commercial adhesive and allowed to dry prior to testing. Indentation depth was limited to 1.5 μm, not exceeding 10% of the total electrode thickness. A continuous stiffness measurement (CSM) was also employed during the loading segment. CSM utilizes a very small oscillating force in order to measure both the instantaneous elasticity and the contact stiffness at all depths. Multiple indentations were performed in order to accommodate for variations in surface roughness, sink-in, and pile-up. Nanoscratch testing followed a commonly employed three-segment profiling technique:^{9,10} pre-profiling at 20 μN for 700 μm, a linear ramp scratch segment between 40–80 mN for 500 μm, and post-profiling at 20 μN. The scratch tip was oriented for face-forward operation, corresponding to orientation (II) as previously described,¹¹ with a horizontal profile velocity set to 10 μm/s. Images were taken in situ with an optical microscope.

Typical load-displacement curves obtained by nanoindentation for the bare and Al₂O₃-coated electrodes are shown in Fig. 1. For identical indentation depths, the peak load that is tolerated by the ALD-coated MoO₃ electrode is twice that of the bare sample. The horizontal plateau represents the viscoelastic creep associated with the PVDF binder.^{12,13} The measured mechanical properties for the bare and coated composite electrodes, together with literature values for PVDF and ALD grown Al₂O₃, are listed in Table I. The bare MoO₃ electrode composite is made up of only 20 wt % binder and exhibits a smaller hardness than bulk PVDF. The significant difference in Young's modulus between the bulk PVDF and composite electrode are attributed to the heavy loading of both MoO₃ nanoparticles (70 wt %) and carbon additive (10 wt %) in the electrode that likely causes scission of the polymer chains. As expected, 300 nm thick, bulk ALD-Al₂O₃ exhibits both a much higher elastic modulus and hardness than the polymer binder. Thus the 150% increase in hardness and 44% increase in Young's modulus of the composite electrode after ALD coating compared to the uncoated electrode (Table I) is not surprising.

The damage imaged by the in situ optical microscope for the bare and ALD-coated electrodes following nanoscratch tests is shown in Fig. 2a and 2b. The scratch direction is from left to right in each image. Complete delamination of the bare electrode from the copper current collector is observed midway during the linear ramp scratch segment for $P_{\max} = 80$ mN. Tip penetration depth also confirms loss of adhesion to the copper substrate for the uncoated electrode, with a force of 80 mN over a scratch length of 600 μm, as shown in Fig. 3. Note that both bare and ALD-coated samples are compared with forces of 40 and 80 mN, and the complete delami-

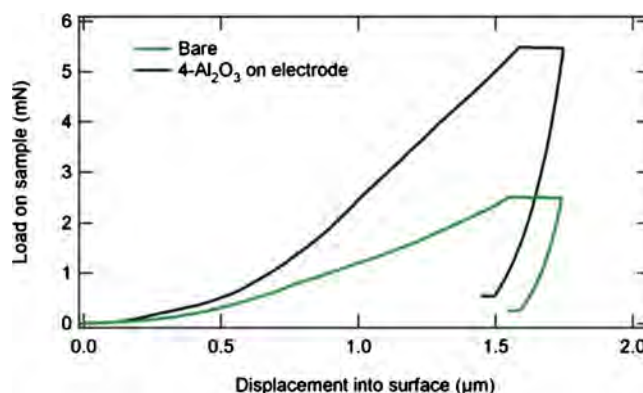


Figure 1. (Color online) Indentation profile for bare and ALD-coated MoO₃ electrodes. The initial loading consists of CSM, followed by a hold to compensate for viscoelastic creep, and finally unloading.

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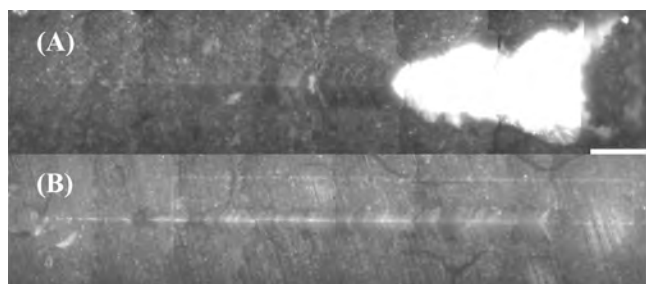
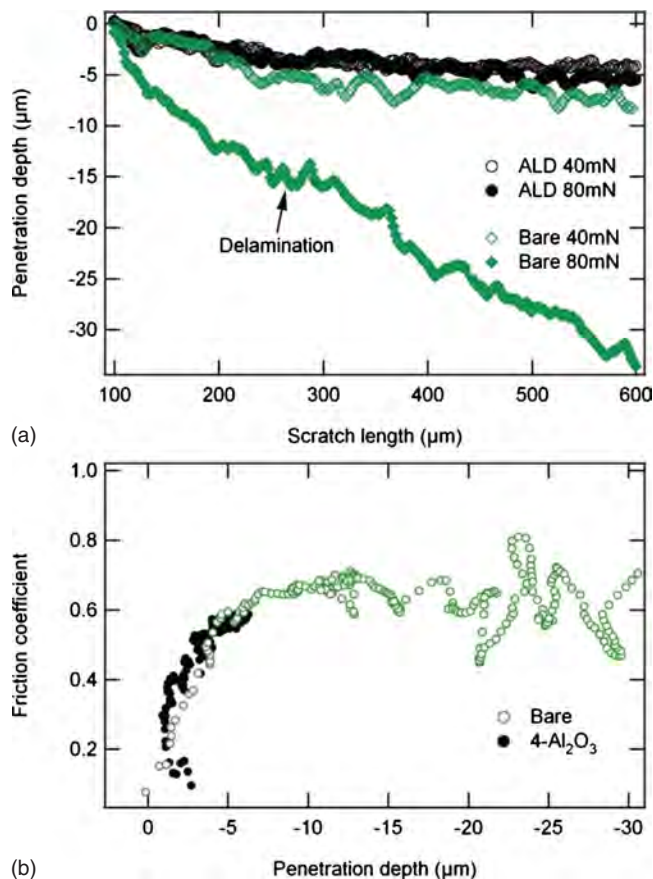
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Table I. Mechanical properties of MoO₃ electrodes during nanoindentation compared to literature values for PVDF and Al₂O₃ films.

	Bare	4-Al ₂ O ₃	PVDF ¹⁴	ALD Al ₂ O ₃ ¹⁵
Modulus from unloading (GPa)	2.16 ± 0.48	3.62 ± 0.66	—	—
Modulus during CSM (GPa)	1.68 ± 0.55	2.68 ± 0.96	3.44 ± 0.14	180 ± 8.2
Hardness (GPa)	0.026 ± 0.01	0.065 ± 0.2	0.24 ± 0.01	12.3 ± 1.0
Stiffness (kN/m)	21.6	32	—	—

nation for the bare sample is denoted with an arrow (Fig. 3a). Notice also that the tip depth at failure (15 μm) is equal to the composite thickness of the bare electrode. Very small penetrations caused by partial-delamination or localized failures are observed for the ALD-coated electrodes in both the 40 and 80 nN tests. Importantly, nei-

**Figure 2.** Optical images of damage caused by nanoscratching with a maximum load of 80 mN for (a) bare and (b) 4-Al₂O₃ ALD-coated MoO₃ composite electrode.**Figure 3.** (Color online) Bare and ALD-coated electrodes tested for (a) depth profile with forces of 40 and 80 mN over a scratch distance of 600 μm and (b) friction coefficient as a function of penetration depth.

ther significant nor complete delamination occurs for the ALD-coated sample, even up to $P_{\text{max}} = 80 \text{ mN}$. Thus, the ALD-coated electrode adheres to the copper substrate for the entire scratch test.

The frictional coefficient (COF) during the linearly increasing application of load is shown in Fig. 3b. COF is defined as a ratio between the force required to move the tip laterally and the load applied normal to the surface.¹⁶ To our surprise, despite the significant differences in mechanical properties observed with nanoindentation, the COF at a given depth remains unchanged after ALD coating. It is known that the lateral force required depends upon both the friction of abrasion between the tip and the surface as well as the friction associated with material adhesion. We therefore speculate that by reducing the elasticity and increasing the electrode brittleness, the Al₂O₃ layer decreases the material adhesion to the scratch tip but increases the friction of abrasion. Conversely, without the coating, the material is noticeably more elastic, resulting in lowering the abrasion between the tip and the composite but increasing the friction due to adhesion. Apparently, these effects compensate such that the two COFs are identical.

In conclusion, we have clearly demonstrated that improved mechanical stability is achieved with the application of only 4 monolayers of alumina to MoO₃ composite electrodes via ALD. After coating, adhesion of the composite electrode on the current collector more than doubles, while the electrode hardness increases by close to 50%. This explains why we have previously observed an improved high-rate electrochemical cycling stability for high volume expansion electrodes coated with ALD.⁸ These results are promising for the implementation of high capacity anodes in commercial Li-ion batteries for next-generation electric vehicles.

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References

1. C. K. Chan, H. L. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, and Y. Cui, *Nature Nanotechnology*, **3**, 31 (2008).
2. C. M. Ban, Z. C. Wu, D. T. Gillaspie, L. Chen, Y. F. Yan, J. L. Blackburn, and A. C. Dillon, *Adv. Mater. (Weinheim, Ger.)*, **22**, E145 (2010).
3. S. H. Lee, Y. H. Kim, R. Deshpande, P. A. Parilla, E. Whitney, D. T. Gillaspie, K. M. Jones, A. H. Mahan, S. B. Zhang, and A. C. Dillon, *Adv. Mater. (Weinheim, Ger.)*, **20**, 3627 (2008).
4. L. A. Riley, S. H. Lee, L. Gedvilas, and A. C. Dillon, *J. Power Sources*, **195**, 588 (2010).
5. J. Li, R. B. Lewis, and J. R. Dahn, *Electrochem. Solid-State Lett.*, **10**, A17 (2007).
6. J. Li, H. M. Dahn, L. J. Krause, D. B. Le, and J. R. Dahn, *J. Electrochem. Soc.*, **155**, A812 (2008).
7. J. H. Lee, W. J. Kim, J. Y. Kim, S. H. Lim, and S. M. Lee, *J. Power Sources*, **176**, 353 (2008).
8. L. A. Riley, A. S. Cavanagh, S. M. George, Y. S. Jung, Y. F. Yan, S. H. Lee, and A. C. Dillon, *ChemPhysChem*, **11**, 2124 (2010).
9. L. Y. Huang, J. W. Zhao, K. W. Xu, and J. Lu, *Diamond Relat. Mater.*, **11**, 1454 (2002).

10. J. Ballarre, E. Jimenez-Pique, M. Anglada, S. A. Pellice, and A. L. Cavalieri, *Surf. Coat. Technol.*, **203**, 3325 (2009).
11. D. Mulliah, D. Christopher, S. D. Kenny, and R. Smith, *Nucl. Instrum. Methods Phys. Res. B*, **202**, 294 (2003).
12. A. M. Vinogradov and F. Holloway, *Polym. Test.*, **19**, 131 (2000).
13. J. F. Mano, V. Sencadas, A. M. Costa, and S. Lanceros-Mendez, *Mater. Sci. Eng., A*, **370**, 336 (2004).
14. W. Y. Chang, T. H. Fang, and Y. C. Lin, *J. Polym. Sci., Part B: Polym. Phys.*, **46**, 949 (2008).
15. M. K. Tripp, C. Stampfer, D. C. Miller, T. Helbling, C. F. Hermann, C. Hierold, K. Gall, S. M. George, and V. M. Bright, *Sens. Actuators, A*, **130–131**, 419 (2006).
16. T. W. Scharf and J. A. Barnard, *Thin Solid Films*, **308–309**, 340 (1997).